New insights into the active sites and the mechanism of methane dehydroaromatization on Mo/ZSM-5

Emiel J.M. Hensen, **Nikolay A. Kosinov**
[a] *Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
**Corresponding author: e.j.m.hensen@tue.nl*

Methane has huge potential as a chemical feedstock as it is an abundant and relatively cheap carbon source with a lower negative environmental footprint than other fossil resources. Despite the clear potential of methane, efficient and industrially applicable direct methane-to-products conversion is not yet available for the chemical industry. In this lecture, I will provide a brief overview of the (catalytic) challenges encountered in developing direct routes for the conversion of methane to chemicals. The activation of methane by metal, metal oxide and other catalytic materials will be discussed in the framework of oxidative and non-oxidative conversion routes. In general, oxidative routes suffer from a low selectivity, whereas catalyst stability is a key challenge in non-oxidative approaches that require high reaction temperatures to overcome thermodynamic limitations. I will specifically discuss recent progress in the understanding of the activation of methane on molybdenum-promoted zeolites and its conversion to aromatics. The nature of the active sites and the importance of a pool of aromatic hydrocarbons to the reaction mechanism of methane aromatization will be discussed. A link will be made to opportunities to directly convert methane to light olefins.

Important challenges in gaining insight into the mechanistic aspects of MDA are the high reaction temperature at which the reaction takes place and its transient nature, which involves rapid activation and deactivation stages when the fresh Mo/ZSM-5 catalyst is exposed to a methane feed. In our research, combining pulse reaction technique, isotope labelling and operando spectroscopy tools it was found that atomically dispersed Mo sites stabilized by the zeolite framework are the active centers for the MDA reaction. Further, we demonstrated that the MDA reaction is governed by a hydrocarbon pool mechanism, in which benzene is derived from secondary reactions of confined polyaromatic carbon species with the initial products of methane activation. Finally, using the molecular understanding of the interactions in the Mo-zeolite system, we developed novel regeneration strategies to optimize the catalytic performance.

References

1. N. Kosinov, A. S. G. Wijpkema, E. Uslamin, R. Rohling, F. J. A. G. Coumans, B. Mezari, A. Parastaev, A. S. Poryvaev, M. V. Fedin, E. A. Pidko and E. J. M. Hensen, Angew. Chem. Int. Ed., 2018, 57, 1016-1020.
2. N. Kosinov and E. J. M. Hensen, in Nanotechnology in Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2017, pp. 469-482.
3. N. Kosinov, F. J. A. G. Coumans, G. Li, E. Uslamin, B. Mezari, A. S. G. Wijpkema, E. A. Pidko and E. J. M. Hensen, J. Catal., 2017, 346, 125-133.
4. N. Kosinov, F. J. A. G. Coumans, E. A. Uslamin, A. S. G. Wijpkema, B. Mezari and E. J. M. Hensen, ACS Catal., 2017, 7, 520-529.
5. N. Kosinov, F. J. A. G. Coumans, E. Uslamin, F. Kapteijn and E. J. M. Hensen, Angew. Chem. Int. Ed., 2016, 55, 15086-15090.